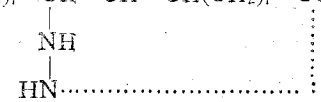
Syntheses of Antioxidants (III) : Polynuclear Alkylphenol Antioxidants Containing p-hydroxyanisole Nuclei and Relations between Molecular Weight and Potencies

AUTHOR(S):

Sisido, Keiiti; Kuyama, Hirosi

(2) The saponified product (Yield; quantitative).

Anal. Calcd. for $(CH_3-(CH_2)_7-CH-CH=CH(CH_2)_7-CO)$:



N, 9.56; Found: N, 10.12.

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15. Syntheses of Antioxidants. (III)

Polynuclear Alkylphenol Antioxidants Containing p-hydroxyanisole Nuclei and Relations between Molecular Weight and Potencies

Keiiti SISIDO and Hirosi KUYAMA

(Sisido Laboratory)

In the preceding report, we have descriced polynuclear alkylphenol antioxidants containing *p*-cresol nuclei and found some excellent, high molecular, active compounds with good solubility to fatty oils. In view of the recent publication that mono-*t*-buty-*p*-hydroxyanisole is an effective and nontoxic antioxidant, we have now prepared some similar polynuclear alkylphenol antioxidants containing *p*-hydroxyanisole and found some effective ones, one of them was superior to commercial 2,6-di-*t*-butyl-*p*-cresol.

p-Hydroxyanisole was dimethylolated as follows. A mixture of 31 g. of p-hydroxyanisole, 100. of of 10 % aqueous NaOH and 37 g. of 40 % formalin was kept at 15-16°C in the period of three days and neutralized with dilute sulfuric acid. After standing overnight in a refrigerator the precipitated crystals were filtered, yield 22 g. Repeated recrystallizations from ethyl acetate afforded pure dimethylol-*p*-hydroxyanisole, m. p. 127-128°C, which was a new compound.

Condensations with various phenols were carried out according to the description of our preceding report. From the condensation product with phenol a crystalline compound was isolated with the aid of hot water and was recrystallized from a mixture of benzene and actic acid, m. p. 192-193°C. The acetate, m. p. 99-100°C, molecular weight, 454. This is considered to be the acetate of a trinuclear compound bis-(p-hydroxybenzyl)-*p*-hydroxyanisole with calculated molecular weight 462. The condensation with *p*-cresol afforded beside resinous product crystals, m. p. 179-181°C, whose acetate, m. p. 120-121°C, had molecular weight of 493. This was assumed to the acetate of trinuclear bis-(2-hydroxy-5-methylbenzyl)-*p*-hydroxyanisole. *o*-Cresol, *m*-cresol, thymol, eugenol, *p*-bromophenol, *o*-bromophenol, *p*-*t*-butylphenol, mono-*t*-butyl-*p*-cresol, mono-*t*-butyl-*o*-cresol and mono-*t*-butyl-*m*-cresol gave resinous products.

Among these, the condensation product with mono-t-butyl-*p*-cresol showed the highest activity, which was superior to commercial 2,6-di-*t*-butyl-*p*-cresol. The condensation products with mono-*t*-butyl-*o*-cresol and mono-*t*-butyl-*m*-cresol, respectively, showed some activities, but other products did not show high activities.

Some of the polynuclear alkylphenols previously reported, that is condensation products of dimethylol-*p*-cresol with *o*-cresol (C-3), thymol (C-5), eugenol (C-6), *p*-hydroxyanisole (C-7), respectively, as well as the condensation product of eugenol and formaldehyde (E-2) were divided into three or four portions with different molecular weights by fractional precipitation with the aid of acetic acid and water. In the case of (C-3), (C-5), (C-6), (C-7), a portion with molecular weight of 300-500 were most effective. An anomaly was observed in the case of (E-2), that is, the monomethylolated product of eugenol, i. e., eugenotine alcohol, m. p. 36°C, was the highest in the activity.

The effects of these compounds to the stability of vitamine A were investigated by G. Katui in the Laboratory of Prof. R. Takata. The results, which coincided with our ones, will be published elsewhere.

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16. Polymerisation of Phenyl Glycide Ether and Thioepichlorohydrin

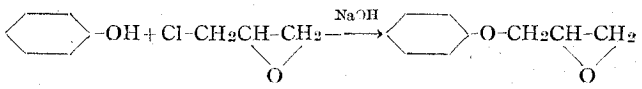
Kiyohisa FURUKAWA and Ryohei ODA

(Oda Laboratory)

A. Phenyl Glycide Ether (P.G.E.)

1) Synthesis

P.G.E. was prepared by the method of Boyd and Marle (J. Chem. Soc., **93**, 838, (1908)) according to the following reaction:



2) Polymerisation

Exp. No.	Polym. temp. (°C)	Polym. time (hr)	Catalyst (%)	Mol. wt. (Cryoscobic method)
1	120~130	18	NaOH (5)	1357
2	〃	79½	〃 (5)	1844
3	80~ 90	18½	〃 (1)	1816
4	120~130	47½	〃 (1)	1279
5	〃	24½	KOH (5)	1531
6	〃	14	〃 (1)	1120
7	〃	65	〃 (1)	923

A brown, soft polymer was obtained, when the monomer was treated with molten and powdered KOH or NaOH as catalyst in a sealed tube. It is im-